Some Reactions of Alkyldifluoramines[1]

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The continuing search for more energetic rocket propellant compositions has focussed attention on several previously unexplored fields of chemistry. Compounds containing fluorine bound to nitrogen offer attractive prospects in such applications. Since effective utilization of any chemical system requires an understanding of the components involved, we have undertaken a study of the reactions of some simple model compounds of this class.

The first synthesis of an N, N-difluoroalkylamine (alkyldifluoramine) in 1936[2] introduced a new family of organic compounds. The perfluoroalkyldifluoramines obtained by fluorination of various carbon-nitrogen compounds[3] have more recently been supplemented by a limited number of analogous compounds containing non-fluorinated alkyl groups.[4] This paper constitutes the first in a series devoted to the study of the chemical properties of these interesting compounds.

Reactions with Organometallic Reagents

Triphenylmethyldifluoramine ("trityldifluoramine", I) has been found to react rapidly with n-butyllithium to yield n-octane and benzophenone anil (II). With equimolar quantities of the reactants the reaction was incomplete and some I was recovered. Only 40% of the fluorine was converted to fluoride ion under these conditions. Increasing the amount of organometallic reagent to two molar equivalents resulted in complete disappearance of the difluoramine; 77% of the total fluorine was recovered as fluoride ion and the yield of II was 70% of theory.

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1. Research reported in this publication was supported by the Advanced Research Projects Agency and administered by the Department of the Navy, Office of Naval Research.

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t-Butyldifluoramine (III) reacted rapidly with either n-butyllithium or phenyllithium to produce n-octane and biphenyl, respectively. Recovery of fluoride ion was 20-27% in equimolar systems and increased to approximately 50% when more than one equivalent of n-butyllithium was used.

Two additional products, present in small quantity, were detected and identified by infrared and mass spectral analyses. These products were azoisobutane (IV) and 1,2-difluoro-1,2-di-t-butylhydrazine (V).

$(CH_3)_3CN{=}NC(CH_3)_3$ IV

$(CH_3)_3CNNC(CH_3)_3$ (F, F) V

The reaction of III with two or four equivalents of n-butyllithium resulted in the formation of a new product, N,N-di-n-butyl-t-butylamine (VI), in yields up to 16% of theory. This previously unknown tertiary amine, b.p. 80-82°/0.3 mm, was identified by infrared and mass spectrometric analyses. A comparison of the mass spectrum of VI with that of the known tri-n-butylamine (Table I) shows that the same major peaks appear, but in quite different relative intensities. The mass peaks due to rearrangements were generally more intense and two such peaks (m/e = 86, 114) which do not occur in tri-n-butylamine were observed.

Table I

Principal Mass Peaks of N,N-n-Butyl-t-Butylamine and Tri-n-Butylamine

m/e	Ionic Species		Relative Intensity $(n\text{-}Bu)_2N\text{-}t\text{-}Bu$	Relative Intensity $(n\text{-}Bu)_3N$[a]
41	$C_3H_5^+$		90	21.4
42	$C_3H_6^+$		34	16.0
43	$C_3H_7^+$		85	7.8
57	$C_4H_9^+$		100	13.4
58	C_4H_{10} or $C_3H_3NH_2$+	(Rearrangement)	75	5.0
72	C_4H_9NH+	(Rearrangement)	91	1.16
86	$C_4H_9NHCH_2$+	(Rearrangement)	92	4.26
99	$C_4H_9N(CH_2)_2$+	(Rearrangement)	12	-----
100	$C_4H_9NH(CH_2)_2$+	(Rearrangement)	8	26.3
113	C_4H_9-N-$(CH_2)_3$+		8	-----
114	C_9H_9-NH$(CH_2)_3$+	(Rearrangement)	4	0.25
128	$(C_4H_9)_2N$+		68	1.03
142	$(C_4H_9)_2NCH_2$+		63	100.0
170	$(C_4H_9)_2NC_3H_6$+		26	0.14
185	$(C_4H_9)_3N$+		8	5.22

a. Mass Spectral Data, A. P. I., Serial No. 1132

The results of this series of experiments are summarized in Table II.

Table II

Reactions of t-Alkyldifluoramines with Organolithium Reagents

Reactants			Products		
RNF_2	R'Li	Molar Ratio	%R'R'	$\%F^-$	Others
I	n-BuLi	1:1	------	40.1	I, II
I	n-BuLi	1:2	present	77.0	I, 42+% II
I	n-BuLi	1:2	------	----	72% II
III	ϕLi	1:1	present	21.1	III, IV, V
III	ϕLi	1:1	50.8	19.5	III
III	n-BuLi	1:1	88.0	25.6	III
III	n-BuLi	1:1	present	25.6	III
III	n-BuLi	1:2	present	48.8	VI
III	n-BuLi	1:4	------	52.0	16.2% VI

Proposed Mechanism of Organolithium Reactions

The various products obtained in the experiments described above can be explained on the assumption that the organometallic reagents reduced the tertiary alkyldifluoramines via a succession of one-electron transfer steps. A possible

$$R_3CNF_2 + R'Li \longrightarrow R_3CNF\cdot + R'\cdot + LiF \qquad (1)$$

I VII a, R = CH_3; b, R = ϕ

$$R_3CNF\cdot + R'Li \longrightarrow R_3CN\cdot + R'\cdot + LiF \qquad (2)$$

VII VIII a, R = CH_3; b, R = ϕ

alternative for the step shown in equation 2 would be interaction of the R' radical derived from the organometallic reagent with the fluoramino radical (VII). Such a process would also produce the nitrene (VIII), but would require different stoichio-

$$R_3CNF\cdot + R'\cdot \longrightarrow R_3CN\cdot + R'F \qquad (3)$$

VII VIII

metry. No trace of the fluorocarbon by-products which would be formed in this process has been detected.

The array of final products obtained in any one experiment was found, as expected, to depend upon the reactant ratio and the order and rate of addition. The reactive intermediate species are capable of interacting in various combinations and products arising from several of these possibilities have been detected.

In each case the hydrocarbon produced by the coupling of two of the radicals derived from the organometallic reagent was a prominent product. Diphenyl and n-octane were obtained from phenyllithium and n-butyllithium, respectively. When an equimolar quantity of phenyllithium was added slowly to t-butyldifluoramine (III), the homogeneous coupling product (V) of the amino radical (VII a) was detected among the products, along with the coupling product (IV) of the nitrene (VIII a). The diradical nature of nitrenes, which leads to dimerization and the production of azo

$$2(CH_3)_3\dot{C}NF \longrightarrow (CH_3)_3CN(F)-N(F)C(CH_3)_3 \quad (4)$$

VII a V

$$2(CH_3)_3C\dot{N}\cdot \longrightarrow (CH_3)_3N{=}N(CH_3)_3 \quad (5)$$

VIII a IV

compounds, is well known.[5] The cross-coupling of VIII a with the n-butyl radical has been observed when an excess of n-butyllithium was used.

$$(CH_3)_3C\dot{N}\cdot + 2CH_3(CH_2)_3\cdot \longrightarrow (CH_3)_3CN(CH_2CH_2CH_2CH_2)_2 \quad (6)$$

VIII a VI

In reactions involving trityldifluoramine (V) rearrangement of the nitrene (VIII b) appears to be favored energetically, since benzophenone anil (II) was the only product found. II has been reported as the principal product of thermal decom-

$$\phi_3C\dot{N}\cdot \longrightarrow \phi_2C{=}N\phi \quad (7)$$

VIII b II

position of tritylazide, N-tritylhydroxylamine, and a number of related compounds[6,7,8] presumably also via the nitrene intermediate. An analogous rearrangement of the t-butyl nitrene (VIII a), if it occurred, would yield the imine (IX) which would be subsequently hydrolyzed to acetone and methylamine. A careful search failed to reveal the presence of any volatile base.

$$(CH_3)_3C\dot{N}\cdot \longrightarrow (CH_3)_2C{=}NCH_3 \xrightarrow{H_2O} (CH_3)_2C{=}O + CH_3NH_2 \quad (8)$$

VIII a IX

5. L. Horner and A. Christmann, Angew. Chem. (Int. Ed.), 2, 599 (1963).
6. Steiglitz, et al., J. Am. Chem. Soc., 36, 272 (1914); ibid., 38, 2081, 2718, 2717 (1916); ibid., 44, 1270, 1293 (1922).
7. L. W. Jones and E. E. Fleck, ibid., 50, 2022 (1928).
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Reactions with Nitric Acid

Since concentrated nitric acid exhibits both oxidative and electrophilic properties, one can anticipate several possible modes of attack on a tertiary alkyldifluoramine. The difluoramine might be protonated and subsequently hydrolyzed, oxidation might produce an amine oxide analog, oxidative cleavage might occur at N-F, C-N, or C-C bonds, or a nitroalkane might be produced. It has been reported, for example, that trityldifluoramine is protonated in concentrated sulfuric acid and decomposes with the liberation of difluoramine.[9] We have confirmed this observation and found, furthermore, that a secondary alkyldifluoramine is similarly protonated but decomposes with the evolution of hydrogen fluoride.[10] Trityldifluoramine has been found to dissolve in glacial acetic acid and to be recovered unchanged upon dilution with water. It was not affected by contact with concentrated hydrochloric acid at room temperature.

The room temperature reactions of t-butyldifluoramine and trityldifluoramine with concentrated nitric acid, in both equimolar quantities and with a large excess of acid, have been studied. Table III presents a summary of the products obtained in each case, as determined chiefly by infrared spectral evidence.

Table III

Reactions of Alkyldifluoramines with 70% Nitric Acid

	t-Butyldifluoramine		Trityldifluoramine	
Product	Equimolar acid	Excess acid	Equimolar acid	Excess acid
NO_2	-------	Large	Present	Large
N_2O	Present	Present	-------	Present
CO_2	-------	Large	-------	-------
NO_3F	Trace	Trace	-------	Trace
NOCl or NO_2F	-------	-------	-------	Trace
SiF_4	Present	Present	-------	Present
Alkylnitrate	Present	Present	-------	Present
Alkylnitrate	-------	Present	-------	Present
Nitroalkane	-------	-------	-------	Present
Carbinol	-------	-------	-------	Major
Alkyldifluoramine	Present	-------	Major	-------

Several points are worth considering in some detail. The large amount of nitrogen dioxide obtained when excess acid was used is apparently the result of decomposition of nitric acid catalyzed by the difluoramine or one of the reaction products. This interpretation is supported by the fact that the quantities of gas obtained were greatly in excess of stoichiometric, based on the difluoramine, and by the observed exponential pressure rise following a protracted induction period.

9. W. H. Graham and C. O. Parker, J. Org. Chem., 28, 850 (1963).
10. Unpublished experiments, this laboratory.

The presence of carbon dioxide among the products of the reaction of t-butyldifluoramine with excess nitric acid is a clear indication that C-C bond cleavage occurred. The nitrate and nitrite esters produced in this experiment were mixtures of various alkyl derivatives, and not solely t-butyl derivatives as in the other cases where nitrate esters were detected. The relative stability of trityldifluoramine toward oxidative cleavage is fully in accord with known differences between aromatic and aliphatic systems.

The appearance of silicon tetrafluoride during an investigation of organic fluorine compounds in glass equipment is generally understood to imply the transient formation of hydrogen fluoride; this interpretation should be applied here. An interesting point, not yet fully understood, is the appearance of nitroalkane and carbinol only in the reaction of trityldifluoramine with excess acid.

In general, the results observed are best understood as the consequences of electrophilic attack on the alkyldifluoramines. The fact that such attack did not occur when trityldifluoramine was treated with hydrochloric acid, an even stronger electrophile, tends to cloud this simple picture. It becomes necessary to invoke the simultaneous participation of an oxidative process in some way which is not yet clear.

Assuming that protonation of the alkyldifluoramine does occur, elimination of difluoramine and formation of a tertiary carbonium ion would logically follow.

$$R_3CNF_2 + H^+ \longrightarrow R_3\overset{+}{C}NF_2H \qquad (9)$$

$$R_3\overset{+}{C}NF_2H \longrightarrow R_3C^+ + HNF_2 \qquad (10)$$

The failure of difluoramine to appear among the final products is not particularly surprising. In the presence of nitric acid and/or nitrogen oxides, it might easily be oxidized and may well constitute the source of the silicon tetrafluoride. The formation of a carbonium ion from trityldifluoramine would be favored by resonance stabilization. In the t-butyl case, on the other hand, this driving force is not present and formation of the ion would be expected to occur less readily. In addition, both the t-butyl carbonium ion and the difluorammonium ion from which it is derived would be more subject to a variety of side reactions than the corresponding trityl species.

Reaction of the carbonium ion with water or with nitrate ion would produce the carbinol and the ester, respectively. Alternatively, the carbinol might be

$$R_3C^+ + H_2O \longrightarrow R_3COH + H^+ \qquad (11)$$

$$R_3C^+ + NO_3^- \longrightarrow R_3CONO_2 \qquad (12)$$

$$R_3COH + HNO_3 \longrightarrow R_3CONO_2 + H_2O \qquad (13)$$

esterified by nitric acid. For the reasons cited above these reactions contributed substantially to the overall result only in the trityldifluoramine reactions.

Experimental

Materials - The phenyllithium and n-butyllithium used in this work were commercial products supplied by Foote Mineral Company in ether-benzene and hexane solutions, respectively. Trityldifluoramine was obtained from Pennisular Chem Research and purified by recrystallization from methanol, m.p. 80-81.5° (uncorr.). t-Butyldifluoramine was prepared by the method of Smith and Castellano[4d] and stored under prepurified nitrogen. The quantity desired for each experiment was distilled from the storage bulb under vacuum and was measured by volume as a gas, assuming ideality. It was condensed directly into the reaction flask from the vacuum line.

Reaction of t-Butyldifluoramine with Phenyllithium

t-Butyldifluoramine (0.55 g., 0.005 mole) was dissolved in 10 ml. of sodium-dried ether and the solution was cooled to 0-5°. In a dropping funnel under nitrogen, 2.5 ml. (0.005 mole) of phenyllithium solution in benzene-ether (Lithium Corporation of America) was diluted with dry ether to 10 ml. This solution was added to the stirred difluoramine solution during one hour. A red-brown color appeared and deepened gradually during the addition. A gentle stream of nitrogen was passed through the reaction flask and then bubbled into a standardized solution containing 5.27 meq. of acid, while 20 ml. of distilled water was added dropwise to the reaction mixture (20 min.). Stirring was continued for one hour. The acid solution was titrated with base and 5.19 meq. was found. The decrease (1.5%) was not considered to be significant. The aqueous and organic phases of the reaction mixture were separated. The water layer was washed with 15 ml. of ether. The wash and the organic layer were combined and washed with three 10 ml. portions of distilled water. These washes were combined with the aqueous solution, which was subjected to analyses as discussed above.

The ether-benzene solution was dried first over Drierite and then over anhydrous sodium sulfate and distilled at atmospheric pressure. The flask was heated in a bath at 55-60° throughout distillation of the bulk of the solvents and raised to 95-100° for 20 min. at the end. A brown tarry residue weighing 1.10 g. remained. The distillate was collected at Dry Ice temperature to avoid the loss of unreacted t-butyldifluoramine or low-boiling products. The mass spectrum of the "non-volatile" fraction contained peaks at 33(NF), 41 (C_3H_5), 45 (CNF), and 57 (C_4H_9) mass units. The trace of ether observed (m/e = 59) was not sufficient to account for the intensity of the peak at 57, to be attributed to t-butyldifluoramine. The most probable source of these fragments is the substitutes hydrazine (V).

The several components of the less volatile fraction were separated by vapor phase chromatography, using a Perkin-Elmer Model 154 C instrument. The six-foot column was packed with di-n-decyl phthalate on firebrick and was maintained at 90° with a helium flow rate of 53 ml/min. Since fractions were expected to be too small to be collected individually, the effluent stream was fed directly into the inlet of a Bendix time-of-flight mass spectrometer. In one fraction mass peaks at 57 (C_4H_9), 71 (C_4H_9N), and 85 ($C_4H_9N_2$) units were observed, in relative intensities identical to those found in azoisobutane IV. Reaction of t-Butyldifluoramine with n-Butyllithium.

A solution of 1.1 g. (0.01 mole) t-butyldifluoramine in 10 ml. hexane was treated with 26.0 ml. (0.04 mole) of n-butyllithium solution, by adding the

organometallic reagent dropwise over a one hour period at 5-10°. The dark brown mixture was stirred for 2.5 hrs at 10-25° and then treated with water. The organic solution was separated and dried over anhydrous Na_2SO_4 while the aqueous solution was analyzed and found to contain 0.197 g. (0.0104 mole, 52.0%) of fluoride ion. The solvent was evaporated from the organic solution and the residual brown oil was distilled to yield 0.32 g. of a liquid, b.p. 79-82°/0.3 min. On the basis of infrared and spectral data, the liquid product was identified as N, N, di-n-butyl-t-butylamine.

Reaction of Trityldifluoramine with n-Butyllithium

A solution of 5.9 g. (0.02 mole) of trityldifluoramine, m.p. 80-81°C, in 40 ml. of hexane was cooled to 0° in a 200 ml. three-neck flask while 25.8 ml. (0.04 mole) of n-butyllithium solution was added dropwise with stirring over a 1.5 hr. period. A deep red color developed as the butyllithium came into contact with the hexane solution, but the color changed to a bright yellow on continued stirring at 5-10°. At the completion of the addition, the solution was allowed to come to room temperature and it was stirred at 25° for 2 hr. Water was then added to the mixture, the organic phase was separated, washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated, leaving 5.72 g. of brown semi-solid. The material was kept under 0.5 mm pressure for 1 hr., a liquid nitrogen trap being employed to collect any liquid distillate. A liquid (0.3 g.) was obtained and submitted for infrared analysis. It showed very strong absorptions indicative of O-H, aliphatic C-H, C-CH_3, C-OH and -$(CH_2)_n$>4. In addition, a medium strength band at 1710 cm^{-1} (C=O) was also present.

The residue was recrystallized from MeOH to yield 2.15 g. (42%) of yellow crystals, m.p. 112-113°, which were identified by infrared and elemental analysis as N-phenylimidobenzophenone (benzophenone anil).

Anal. Calcd. for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44.

Found : C, 88.85; H, 5.86; N, 5.61.

The physical constants are in excellent agreement with the literature (m.p. 113-114° [11]).

The methanol solution from the recrystallization was evaporated to dryness to yield 3.3 g. of a mixture of trityldifluoramine and N-phenylimidobenzophenone. In addition, the infrared spectrum of this material showed weak absorptions due to aliphatic C-H, C=O and C-N or C=C.

A solution of 1.48 g. (0.005 mole) of trityldifluoramine in 30 ml. hexane was treated with 6.5 ml. (0.01 mole) of n-butyllithium solution as in Section 1. Water was added to the reaction mixture and the organic phase was separated and washed with four 100-ml portions of distilled water. The combined aqueous washings were transferred to a 500 ml. volumetric flask and adjusted to volume with distilled water. This solution was found to contain 146 mg. F^- (0.0077 mole, 77%) and 0.0028 mole OH^-.

11. Weston and Michaels, J. Am. Chem. Soc., 73, 1381 (1951).

The hexane solution was dried over Na_2SO_4 and the solvent evaporated. The residue was taken up in CH_2Cl_2 and chromatographed on alumina. The chromatogram was followed by the yellow band which moved down the column. This yellow CH_2Cl_2 eluate was evaporated to dryness and the residue was recrystallized from ether to yield 0.92 g. (0.0036 mole, 72%) benzophenone anil, m.p. 112-113°. The column was eluted with MeOH and the solvent was evaporated to give 0.13 g. of brown solid. The infrared spectrum of this material showed strong absorptions indicative of aliphatic C-H, aromatic C-H, C=N or C=O (1660 cm^{-1}), a trace of N-F, and substituted aromatic.

t-Butyldifluoramine and Nitric Acid

1. t-Butyldifluoramine (1.02 g., 9.3 mmoles) was condensed under vacuum into a flask containing 10 ml. (150 mmoles) of concentrated HNO_3. The mixture was warmed to room temperature and stirred. The pressure rose to 210-220 mm. and remained constant for 16 hr. After this period, the pressure rose within 1-1/2 hr. to 730 mm., with the evolution of brown gas. On cooling the reaction flask to -70°, the pressure dropped to 340 mm. A sample of this gas was subjected to infrared analysis and found to contain C-H (3.33/6.75μ), $C-CH_3$ (7.27μ), N_2O (4.5μ), N_2O_4 (5.72/6.15μ), N-F(attributed to starting material, 10.30/11.35μ), NO_3F (10.85/12.65/13.90μ), CO_2 (4.35/15.96μ), SiF_4 (9.75μ), and NOCl (presumably from attack on NaCl window, 5.53/5.58μ). Mass spectrometric analysis confirmed the presence of starting difluoramine, CO_2 and/or N_2O, SiF_4, and NO_3F, and established the absence of H_2 and O_2. A second gas sample taken at 0° was found to contain some of these components, but no additional products. The acid solution was extracted with pentane to remove organic products. Infrared analysis of this extract revealed the presence of alkyl nitrite and nitrate (C-H at 3.51/6.90μ, possible $C-CH_3$ at 7.28μ, C-ONO at 6.41μ, and $C-ONO_2$ at 6.10μ).

2. Concentrated nitric acid (0.67 ml., 10.0 mmoles) was delivered by pipet into a 50 ml. round-bottomed flask, which was fitted with a magnetic stirring bar and a suitable adapter, and attached to a vacuum line. The acid was frozen in a liquid N_2 bath and the flask was evacuated. The acid was melted and refrozen twice, with evacuation to effect degassification. t-Butyldifluoramine (1.09 g., 10.0 mmoles) was evaporated into an evacuated calibrated storage bulb to the calculated pressure and then condensed into the flask with liquid N_2. The reactor portion of the line (with manometer) was closed off, and the flask was allowed to warm to room temperature. The mixture was stirred at 26-29° for 24 hr., during which the pressure remained essentially constant (186-198 mm. Hg). The liquid mixture became yellow, but no brown fumes appeared in the vapor space.

Gas samples for infrared and mass spectral analyses were taken, with the reaction flask at 25° and -78°. Both samples contained an alkyl nitrate, N_2O, t-butyldifluoramine and some additional N-F material, and a trace of NO_3F.

The liquid reaction mixture was extracted with CCl_4. Infrared analysis of the extract did not indicate any additional products. The aqueous residue was evaporated to dryness at room temperature and a few needle crystals were recovered. The infrared spectrum of this solid showed only absorptions due to water. Attempts to dehydrate the small amount of product which remained were unsuccessful.

Trityldifluoramine and Nitric Acid

1. Recrystallized trityldifluoramine (1.0 g., 3.4 mmoles, m.p. 80-81.5°) and a small magnetic stirring bar were placed in the bottom of a reaction tube having a small side chamber. Concentrated (70%) nitric acid (2.5 ml., 38 mmoles) was placed in the side chamber and the tube was connected to a vacuum line by means of standard taper joints. The nitric acid was frozen by immersion in a liquid nitrogen bath and the system was evacuated. The cold bath was removed. Then the tube was rotated so that the nitric acid, as it melted, flowed onto the trityldifluoramine.

The resulting slurry was stirred at 22-25° for 24 hr. The reaction mixture bubbled and became progressively darker and brown fumes were observed in the vapor space. The pressure rose exponentially to reach a maximum of approximately 400 mm. in 2.5 hr. (system volume - 180 ml.) and then remained constant.

After 24 hr., the reaction mixture was cooled to -78°, and a gas sample was taken for analysis, Infrared and mass spectrometric examination revealed the presence of NO_2, N_2O, SiF_4, and either NOCl or NO_2F.

The reaction tube was then warmed to room temperature, flushed with nitrogen, and opened. The reaction mixture was diluted with distilled water (color changed from dark brown to bright orange) and the solid product was removed by filtration. The filtrate was neutralized with Na_2CO_3 (color changed from pale amber to brown) and extracted with benzene. No residue was obtained upon evaporation of an aliquot of the benzene extract. Reacidification of the aqueous layer lightened the color, but not to the original shade. The remaining color was too intense to permit the determination of fluoride ion.

The orange solid product was washed with water, dried in vacuum over P_2O_5, and chromatographed on an alkaline alumina column. The first fraction, 420 mg., yellow to pale orange crystals eluted with pentane-benzene, proved to be the principal constituent of the mixture. It was recrystallized from pentane-benzene to give a nearly colorless compound, m.p. 162.5-163°. Its infrared spectrum was identical with that of triphenylcarbinol (lit.[12] m.p. 162.5°).

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.66; H, 6.20.

Found : C, 87.06/87.21; H, 6.29/6.41.

2. Trityldifluoramine (2.95 g., 10 mmoles) was placed, along with a small magnetic stirring bar, in a test tube having a standard taper glass joint. The tube was flushed with dry nitrogen and placed in a liquid nitrogen bath. Concentrated HNO_3 (0.67 ml., 10 mmoles) was introduced slowly and allowed to freeze on the side of the tube without contacting the trityldifluoramine. The reaction tube was then connected via a suitable adapter to a vacuum system, evacuated, and allowed to warm to room temperature. After the mixture was stirred for 18 hr. at 25-28°, a sample of the gaseous products (p = 55 mm. in 180 ml.) was taken in an evacuated cell. The system was then filled with nitrogen to atmospheric pressure. The reaction mixture was diluted with distilled water and the yellow insoluble product was removed by filtration. The yellow aqueous filtrate was extracted three times with methylene chloride, the third extract contained very little color, although the

12. N. A. Lange, Handbook of Chemistry

aqueous solution remained a strong yellow. On standing, the combined extracts became orange in color, as did the solid product on the filter.

Infrared analyses of the gas sample and the methylene chloride extract (differential vs. solvent) showed no significant absorptions. The aqueous solution was found to contain 7.41 meq. of free acid and 25 mg. (1.3 meq.) of fluoride ion. The infrared absorption spectrum of the bright yellow-orange solid (m.p. 79-81°) was superimposable upon that of trityldifluoramine.

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